

# Carbon-tolerance effects of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ modified Ni/YSZ anode for solid oxide fuel cells under methane fuel conditions

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**Abstract** Samarium-doped ceria (SDC) is coated onto a Ni/yttria-stabilized zirconia (Ni/YSZ) anode for the direct use of methane in solid-oxide fuel cells. Porous SDC thin layer is applied to the anode using the sol–gel coating method. The experiment was performed in  $\text{H}_2$  and  $\text{CH}_4$  conditions at 800 °C. The cell performance was improved by approximately 20 % in  $\text{H}_2$  conditions by the SDC coating, due to the high ionic conductivity, the mixed ionic and electronic conductive property of the SDC, and the increased triple phase boundary area by the SDC coating in the anode. Carbon was hardly deposited in the SDC-coated Ni/YSZ anode. The cell performance of the SDC-coated Ni/YSZ anode did not show any significant degradation for up to 90 h under  $0.1 \text{ A cm}^{-2}$  at 800 °C. The porous thin SDC coating on the Ni/YSZ anode provided the electrochemical oxidation of  $\text{CH}_4$  over the whole anode, and minimized the carbon deposition by electrochemical carbon oxidation.

**Keywords** Solid oxide fuel cell · SDC coating · Methane · Electrochemical oxidation · Carbon deposition

## 1 Introduction

Solid oxide fuel cells (SOFCs) have been studied as a promising energy conversion system due to their high energy efficiency and fuel flexibilities. The high operation temperature (800–1,000 °C) enables operation with direct hydrocarbon fuels, including natural gas, coal gasified fuels, gasoline, and diesel [1–5]. The fuel flexibilities reduce the operation costs of the SOFC system by elimination of the high-grade purifying process and direct use of economically derived fuels without an additional external reforming process. Ni/YSZ anodes have been known as excellent reforming catalytic materials in anodes for fuel oxidation, and as good electronic conductive materials for use as a typical anode. However, the use of practical hydrocarbon fuels such as natural gas or syn-gas inhibits catalysis in the Ni/YSZ anode via carbon coking and sulfur poisoning, leading to losses in cell performance [6–9]. In addition, carbon can be deposited in the anode pores and block the pathway of fuels, leading to gas diffusion resistance [7, 10]. The anode structure can be disrupted by carbon deposition diffusing into the nickel phase, leading to permanent structural damage of the cell. In order to prevent carbon coking, numerous research efforts have been made regarding the effects of carbon deposition, and for developing alternative anodes for the utilization of practical hydrocarbon fuels [11–14].

Practical hydrocarbon fuels, typically methane, can be used by internal steam reforming to produce hydrogen and carbon monoxide in a Ni-based anode, because Ni is catalytically active as a steam reforming catalyst. In previous

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research, Ni-based anodes were reported as direct internal steam reforming materials [15–18]. Steam reforming, however, has limitations for operation in SOFCs, even though there may be satisfactory results. The reaction is highly endothermic, which affects the temperature control for the system, and requires a high steam-to-carbon ratio to avoid carbon formation. For intermediate-temperature SOFCs (IT-SOFCs), one of the promising approaches for SOFC technology, direct-steam reforming might not be a suitable option because of the endothermic reaction. Another method to utilize hydrocarbon fuels is dry reforming (also called  $\text{CO}_2$  reforming) [19, 20]. To avoid carbon deposition in dry reforming, however, excess  $\text{CO}_2$  in the feed is suggested, which leads to lower hydrogen yield and electrical efficiency.

Developing Ni-free and carbon-resistant alternative anode materials is one way to utilize hydrocarbon fuels. There are a number of strict requirements for alternative SOFC anode materials. The anodes are electro-catalytically active for the oxidation of hydrocarbon fuel. The anodes are both ionically and electronically conductive. They must be stable in reducing conditions at high temperature. They also must resist carbon deposition and sulfur poisoning, and chemically compatible with the electrolyte. Gorte et al. [4, 9] successfully developed a Cu– $\text{CeO}_2$ –YSZ anode where Cu provides electronic conductivity without catalyzing carbon formation in the direct electrochemical oxidation of various hydrocarbons, with  $\text{CeO}_2$  providing catalytic activity. MIEC materials with perovskite structure, such as  $\text{La}_x\text{Sr}_{1-x}\text{Cr}_y\text{Mn}_{1-y}\text{O}_{3-\delta}$ ,  $\text{Y}_x\text{Sr}_{1-x}\text{TiO}_3$ , and  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ , have recently been suggested as anode materials to utilize hydrocarbon fuels [21–24].

The SDC research, as an alternative SOFC anode, has been widely studied. Our research, however, is different from them in coating method. The major difference from previous research is coating method; they were using infiltrated or impregnated method to coat the electrode surface which led to uncontinuous coating layer. Otherwise, we used dip-coating method which led to continuous coating layer. Normally, infiltration method is used to make a catalyst which has a structure of catalytic material well dispersed on a support material. Therefore, the impregnation or infiltration method is not good for a continuous film formation. We have already reported that the continuous and porous oxygen-ion conductive film can increase the TPB sites in both cathode and anode [24–26].

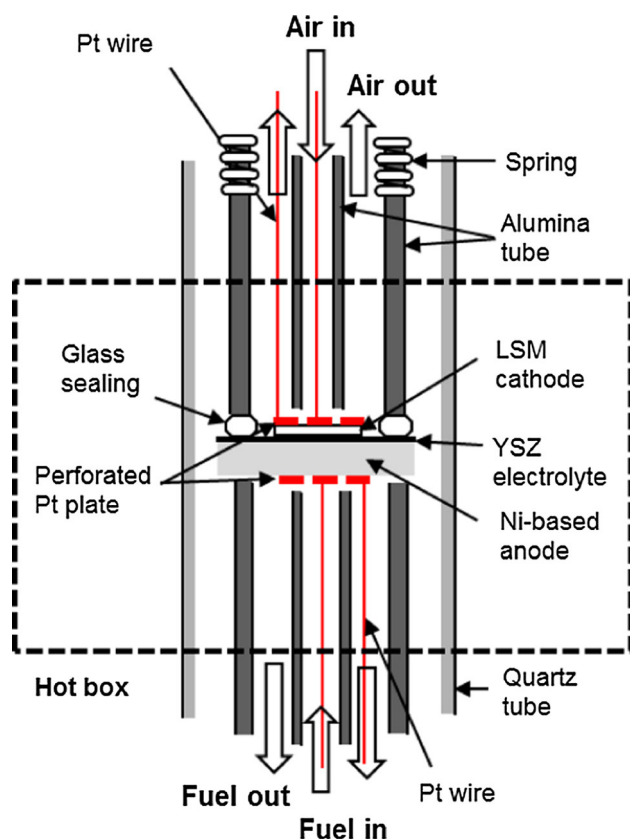
In this study, porous SDC film was coated onto Ni/YSZ anode as an alternative anode material for using methane fuels. The SDC-modified anode was compared to the conventional Ni/ $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_2$  (Ni/YSZ) anodes. Because of the high ionic conductivity of SDC, the deposited carbon in the TPB area can be oxidized more readily than that in the Ni/YSZ anode [25, 26]. The thin, porous SDC layer on the

Ni surface can protect the anode from carbon formation, and improve the cell performance due to the additional TPB area. The continuous SDC coating layer applied by dip coating could provide individual ionic paths (through a continuous SDC layer) and electronic paths (Ni phase). The deposited carbon on the TPB site can be readily oxidized by oxygen ions over the whole anode surface due to the thin SDC layer coated on the anode.

## 2 Experimental

The SDC sol was prepared by diluting a commercial  $\text{CeO}_2$  colloidal dispersion (0.01–0.02  $\mu\text{m}$  particles in  $\text{H}_2\text{O}$ , Alfa Aesar) in distilled water. Samaria nitrate ( $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.9 %, Aldrich), diluted in distilled water, was slowly added to the dilute ceria sol, while stirring the solution in order to make 20 mol% samaria-doped ceria ( $(\text{CeO}_2)_{0.8}(\text{Sm}_2\text{O}_3)_{0.2}$ ) sol. To investigate the carbon deposition in the anodes, two different types of electrolyte-supported cells were prepared for an unmodified (bare) Ni/YSZ anode and an SDC-modified Ni/YSZ anode. The electrolyte supports were made by the uniaxial pressing method (Carver Press Inc., USA) with an 8 mol% commercial  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  powder (TZ-8YS, Tosoh) and sintered at 1,400 °C for 2 h to prepare a disk-type cell. For the anode, Ni/YSZ slurry was prepared by mixing 70 wt% NiO powder (Samchun Chemical Inc., Korea) and 30 wt% YSZ powder (TZ-8YS, Tosoh) with a PMMA pore former, binder, and other additives. The NiO/YSZ slurry was coated on the dense 8YSZ electrolyte surface with the tape-casting method and co-firing with the electrolyte at 1,450 °C for 5 h.  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  (LSM) paste was coated as a cathode material on the 8YSZ electrolyte with a screen-printing method and fired at 1,100 °C. The single cells were 1.4-mm thick and 25.4 mm in diameter. The active areas of the cathode and anode were 1  $\text{cm}^2$ , and the thickness of the anode was approximately 30  $\mu\text{m}$ . To modify the anode pore wall surface, the Ni/YSZ anode was dip coated in the prepared SDC sol for 24 h at room temperature and then calcinated at 700 °C for 2 h in air. To maximize the modification effect on the anode pore wall surface, the coating and calcination process were repeated five times. To minimize the cathode effects from the SDC coating, the cathode side was masked completely during the anode coating process.

To investigate the electrochemical performance, a disk-type cell was mounted between double-layered alumina tubes and sealed with Pyrex glass on the dense electrolyte, as illustrated in Fig. 1. The equipment settings have been described previously in more detail [24]. The experiment was performed with a flow rate of 200  $\text{ml min}^{-1}$  of humidified  $\text{H}_2$  or humidified  $\text{CH}_4$  for the anode gas, and excess air for the cathode gas at 800 °C. The microstructure of the SDC-modified Ni/YSZ anode and the carbon

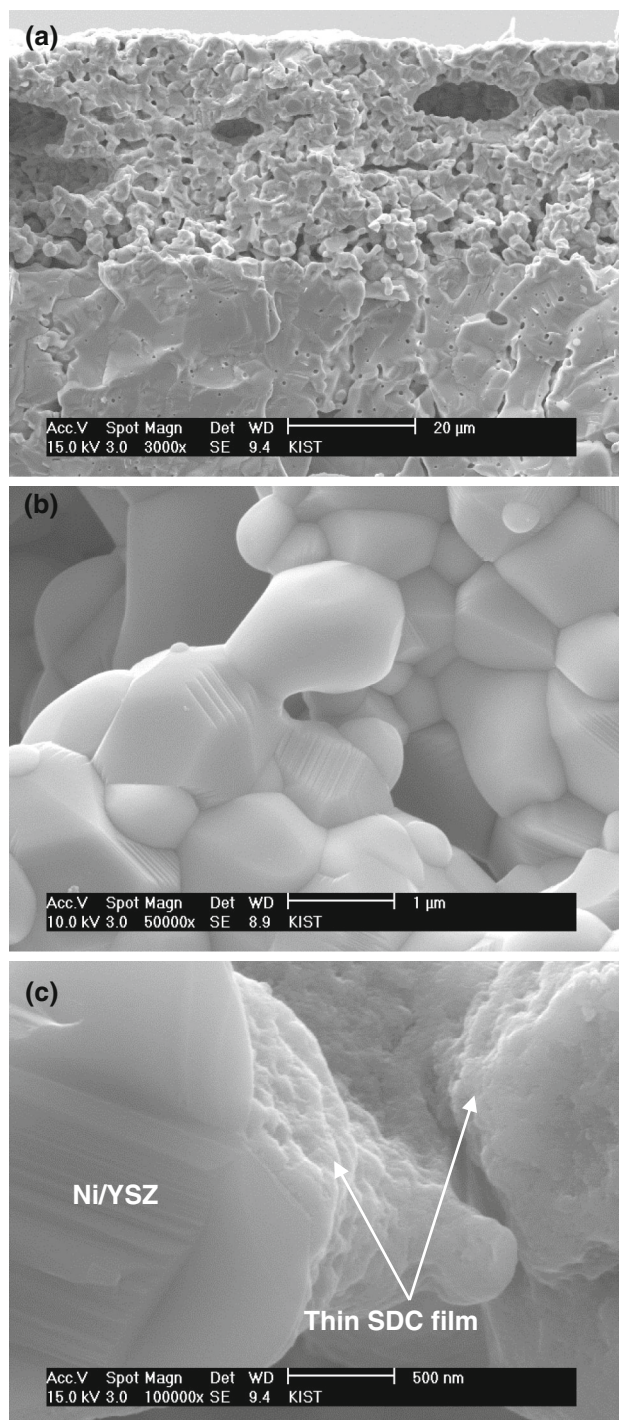


**Fig. 1** Schematic of the experimental setup for a cell mounting

formation was analyzed with an electro-probe microanalyzer (FE-EPMA, JXA-8500F, JEOL Ltd. Japan) and an X-ray diffractometer (XRD, Rigaku, RINT-5200). The impedance spectra were recorded in the frequency range of  $10^{-2}$ – $10^6$  Hz, with an excitation voltage of 10 mV to ensure a linear response. The impedance analyses were performed at 800 °C, and the Nyquist plot obtained indicated an equilibrium state. A DC electronic loader was used to investigate the cell performance drop due to carbon deposition on the Ni-based anode.

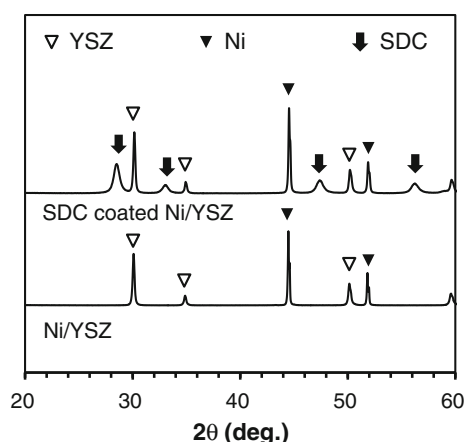
### 3 Result and discussion

SDC has good oxygen conductive properties as well as mixed ionic and electronic conductive (MIEC) properties in reducing conditions [27]. The high oxygen conductive properties can improve the transportation of oxygen ions from the electrolyte to the TPB in the electrode. The MIEC properties can provide additional electrochemical reaction area beyond the TPB sites. Due to these benefits as an SOFC anode material, SDC has been known as an alternative anode candidate. SDC sol was coated on a Ni/YSZ anode wall surface to inhibit carbon deposition in the anode and to improve the cell performance under methane fuel



**Fig. 2** SEM cross-sectional images for interface of Ni/YSZ and YSZ electrolyte (a) and the nanostructural analysis of the unmodified Ni/YSZ anode (b) and the SDC-coated Ni/YSZ anode (c)

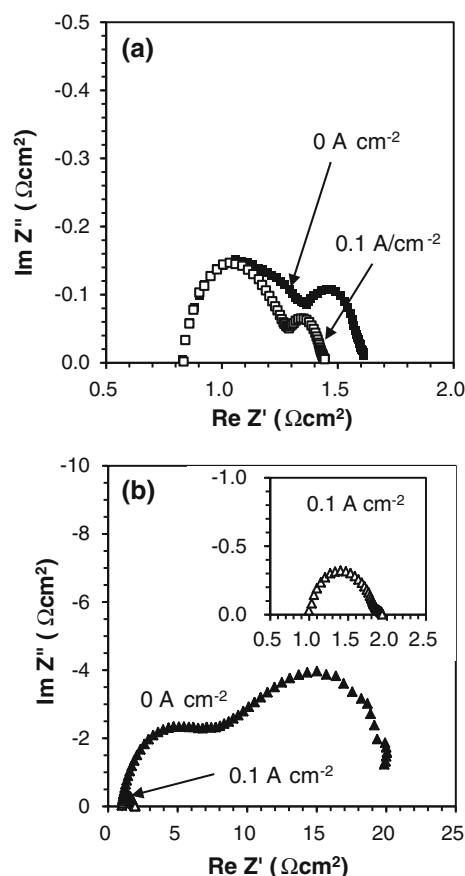
conditions. The electrochemical reaction can occur on the whole surface of the anode by the continuous and porous SDC thin coating layer on the anode pore wall surface. Cross-sectional views of the anode microstructure for the Ni/YSZ anode and the SDC-modified Ni/YSZ anode are shown in Fig. 2. The interface of Ni/YSZ anode and YSZ



**Fig. 3** XRD analysis of the Ni/YSZ (bottom) and the SDC-coated Ni/YSZ (top)

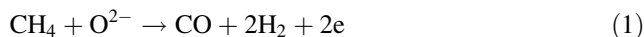
electrolyte is also shown in Fig. 2a. The thickness of the YSZ electrolyte and that of the Ni/YSZ anode is around 1.4 mm and 35  $\mu\text{m}$ , respectively. The SDC thin film was coated continuously on the Ni/YSZ anode. The thickness of the SDC film was 10–50 nm. For the SDC-modified Ni/YSZ anode, XRD analysis was performed to identify the by-products during the SDC coating process, as shown in Fig. 3. Additional by-product patterns were not detected, but the patterns of Ni, YSZ, and SDC were clear.

To investigate the SDC coating effect on the Ni/YSZ anode, impedance spectra of an unmodified Ni/YSZ anode were investigated under  $\text{H}_2$  and  $\text{CH}_4$  conditions as shown in Fig. 4. The SDC-modified anode was also analyzed under  $\text{H}_2$  and  $\text{CH}_4$  conditions, as shown in Fig. 5. For the  $\text{CH}_4$  condition, the NiO/YSZ anode was treated in  $\text{H}_2$  to reduce NiO phase to Ni phase for 5 h at 800  $^\circ\text{C}$ . The impedance spectra of  $\text{CH}_4$  condition were collected 30 min after changing the fuel gas at 800  $^\circ\text{C}$ . The carbon would be deposited continuously with time, especially in the Ni/YSZ anode. Therefore, impedance spectra data were acquired exactly 30 min after changing the fuel gas. The initial impedance spectra of  $\text{H}_2$  gas are shown in Figs. 4a and 5a under open circuit voltage (OCV) and 0.1  $\text{A cm}^{-2}$  current condition. Then, the cell was exposed to the  $\text{CH}_4$  gas for 30 min under OCV and current condition and the impedance spectra were collected as shown in Figs. 4b and 5b. To analyze the conductive effect of oxygen ions, the cells were analyzed under current conditions of 0.1  $\text{A cm}^{-2}$  and compared to OCV conditions. The cell was measured. Single cells with an LSM cathode |8YSZ electrolyte| Ni/YSZ anode configuration were used for the impedance analysis. The cell was tested at 800  $^\circ\text{C}$  with a flow of  $\text{H}_2$  (200  $\text{ml min}^{-1}$ ) in the anode and excess air in the cathode. For the unmodified Ni/YSZ anode, the polarization resistances with  $\text{H}_2$  fuel were 0.78 and 0.61  $\Omega \text{ cm}^2$  under 0 and 0.1  $\text{A cm}^{-2}$ , respectively. With  $\text{CH}_4$  fuel, the polarization



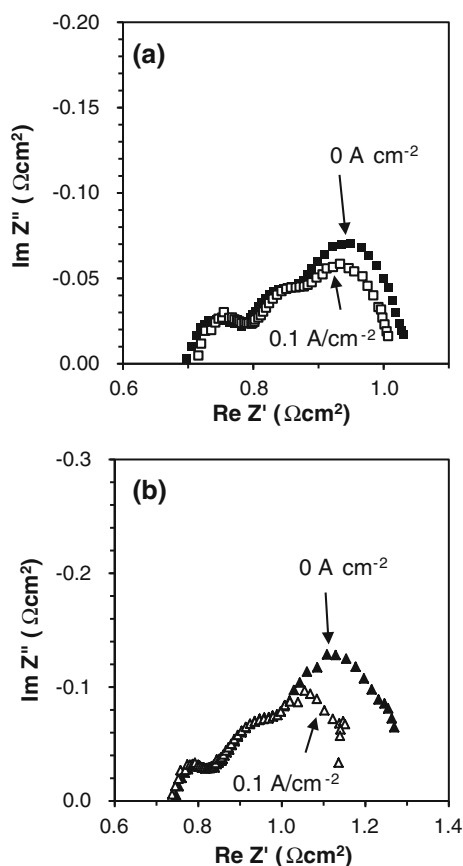
**Fig. 4** Comparison of impedance spectra for the Ni/YSZ anode under  $\text{H}_2$  conditions (a) and  $\text{CH}_4$  conditions (b) at 800  $^\circ\text{C}$

resistance was significantly increased to 18.9  $\Omega \text{ cm}^2$  under 0  $\text{A cm}^{-2}$  because of carbon deposition in the anode. Otherwise, under current conditions of 0.1  $\text{A cm}^{-2}$ , the polarization resistance was increased to 0.94  $\Omega \text{ cm}^2$ . The oxygen ions can react with the deposited carbon electrochemically under current conditions. The possible reaction mechanisms of the carbon deposition and the regeneration via direct electrochemical reaction can be given by:



Reaction (1) is the direct electrochemical oxidation of methane. Previous research suggested that the direct electrochemical oxidation of methane was likely to occur in  $\text{CH}_4$ -rich conditions [24, 25]. Methane could be oxidized partially by oxygen ions to form carbon monoxide via the direct electrochemical oxidation of methane (reaction 1). The pyrolysis of methane could occur in the Ni/YSZ anode, leading to carbon deposition (reaction 2). The carbon deposited on the Ni surface can prevent the catalytic activity of Ni/YSZ cermet and block the anode pores,





**Fig. 5** Comparison of impedance spectra for the SDC-coated Ni/YSZ anode under  $\text{H}_2$  conditions (a) and  $\text{CH}_4$  conditions (b) at  $800^\circ\text{C}$

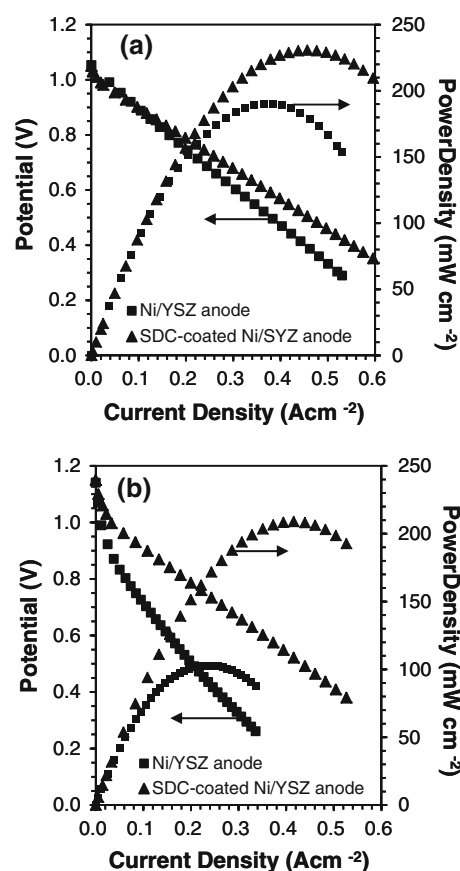
leading to a decrease in cell performance. In addition, the carbon can diffuse readily into the bulk nickel phase and disrupt the anode structure. The deposited carbon can be oxidized electrochemically at the TPB sites via reaction (3). Therefore, the carbon deposition on the anode via reaction (1) can be competed with the regeneration of nickel via reaction (3). For the unmodified Ni/YSZ anode, the carbon deposition can occur on the nickel surface, and the regeneration via electrochemical oxidation of carbon can only occur at the TPB sites. For the SDC-modified Ni/YSZ anode, regeneration occurred on the whole anode surface, because the thin, porous SDC layer was coated on the whole Ni/YSZ anode due to the mixed ionic and electronic conductive properties of the SDC. Figure 5 shows the impedance spectra of the SDC-modified Ni/YSZ anode in  $\text{H}_2$  and  $\text{CH}_4$  conditions. A current of  $0.1 \text{ A cm}^{-2}$  was also applied and compared to the OCV conditions. The polarization resistances in the SDC-modified Ni/YSZ anode under OCV conditions were  $0.33$  and  $0.52 \Omega \text{ cm}^2$  in  $\text{H}_2$  and  $\text{CH}_4$  conditions, respectively. Under  $0.1 \text{ A cm}^{-2}$ , the polarization resistances were  $0.29$  and  $0.39 \Omega \text{ cm}^2$  in  $\text{H}_2$  and  $\text{CH}_4$  conditions, respectively. Even though the electrochemical reactions that occurred in the anode are

very complicated and the reaction mechanisms are difficult to analyze, the SDC modification effect was distinct, in that the polarization resistance was significantly reduced in the SDC-modified anode under both OCV and current conditions. The coverage of the SDC thin layer on the Ni/YSZ anode provides less chance of the carbon deposition on the Ni phase in the anode. The SDC thin layer coating might not only provide additional reaction area beyond the TPB sites from the MIEC properties of the SDC, but also the surface extension of TPB sites by surface modification could also reduce the electrode polarization resistance.

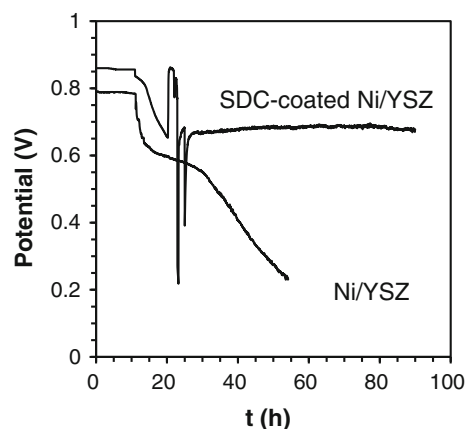
Figure 6 shows the I–V characteristics of the electrolyte-supported single cell with the unmodified Ni/YSZ anode and the SDC-modified Ni/YSZ anode in  $\text{H}_2$  and  $\text{CH}_4$  conditions at  $800^\circ\text{C}$ . After stabilizing the cell in either  $\text{H}_2$  or  $\text{CH}_4$  for approximately 30 min at  $800^\circ\text{C}$ , the I–V characteristics were measured with  $200 \text{ ml min}^{-1}$  of  $\text{H}_2$  or  $\text{CH}_4$  gas in the anode and excess air in the cathode. The initial cell performance is shown in Fig. 6a, and then the cell was exposed to the  $\text{CH}_4$  fuel during 30 min. Because the carbon deposition would be continuously occurred in  $\text{CH}_4$  fuel condition, especially in the Ni/YSZ anode, we collected impedance spectra 30 min after changing the fuel gas as shown in Fig. 6b. The maximum cell performance was  $190 \text{ mW cm}^{-2}$  for the unmodified Ni/YSZ anode and  $231 \text{ mW cm}^{-2}$  for the SDC-coated Ni/YSZ anode. For the SDC-coated Ni/YSZ anode, the performance improved by approximately 20 % compared to the unmodified Ni/YSZ anode, due to its high ionic conductivity and electrochemical catalytic activity, as well as by extending the TPB area. Depending on the temperature and oxygen partial pressure,  $\text{CeO}_2$  exhibits a large oxygen deficiency with the formula  $\text{CeO}_{2-\delta}$  ( $0 < \delta < 0.3$ ) leading to increase electronic conductivity ( $\text{Ce}^{4+}$  ion to  $\text{Ce}^{3+}$  ion). In spite of the tendency to be reduced in a reducing environment, doped ceria has been considered as SOFC electrolyte, because of its high ionic conductivities. The radius  $\text{Ce}^{4+}$  in  $\text{CeO}_2$  is sufficiently large that a variety of dopant can be incorporated [28]. As a consequence, the ionic conductivity for oxygen ions can be increased in doped ceria, leading to improvement in the cell performance. In addition, the effective electrolyte area can be extended by increasing the contact area between the electrolyte and the anode with an SDC modification. Therefore, more oxygen ions from the electrolyte can likely transfer to the anode through the continuous SDC pathway. In the presence of  $\text{CH}_4$  gas in the anode, the maximum cell performance was  $103 \text{ mW cm}^{-2}$  for the unmodified Ni/YSZ anode and  $209 \text{ mW cm}^{-2}$  for the SDC-coated Ni/YSZ anode. For the unmodified Ni/YSZ anode, the maximum cell performance was significantly decreased by around 40 % in  $\text{CH}_4$  condition. Otherwise, the maximum cell performance was decreased by only around 10 % in the SDC-coated Ni/YSZ anode.

The pyrolysis of methane via reaction (2) could be the governing reaction in the unmodified Ni/YSZ anode, even though the methane and the deposited carbon gas could be electrochemically oxidized via reactions (1) and (3). The TPB sites could be deactivated, and the anode pores could be blocked by the carbon particles deposited in the Ni phase. Also, the relatively low ionic conductivity of YSZ could limit the electrochemical oxidation of carbon via reaction (3) in the TPB site. For the SDC-coated Ni/YSZ anode, the higher ionic conductivity and additional reaction sites beyond the TPB from the mixed ionic and electronic conductivity exhibited in the SDC phase may explain the improved performance in  $\text{CH}_4$  of the SDC-coated Ni/YSZ anode compared to the unmodified Ni/YSZ anode. Therefore, the electrochemical oxidation via reaction (1) was more likely to occur in the SDC-coated Ni/YSZ anode than in the unmodified Ni/YSZ anode. Although the carbon deposition in the nickel phase can also occur through methane pyrolysis in the Ni/YSZ and the SDC-coated Ni/YSZ anode, the deposited carbon in the SDC-coated Ni/YSZ anode can more likely be removed in the TPB site, due to the high ionic conductivity of SDC, through the electrochemical oxidation of carbon via reaction (2). Moreover, the porous SDC layer coated on the pore surface of the Ni/SDC anode could protect the nickel surface from the methane, leading to the limited pyrolysis of methane on the nickel surface.

To analyze the long-term stability of the unmodified Ni/YSZ anode and the SDC-coated Ni/YSZ anode, the performance of the YSZ electrolyte-supported single cell was measured under a constant current of  $0.1 \text{ A cm}^{-2}$  at  $800^\circ\text{C}$ , as shown in Fig. 7. After 10 h of stabilizing the cell in humidified  $\text{H}_2$ , the humidified  $\text{CH}_4$  was introduced as an anode fuel. The cell performance of both anodes was rapidly decreased for the first few hours. For the Ni/YSZ anode, the cell performance dropped significantly from 0.76 to 0.6 V at the first drop stage, and then it decreased continuously. For the SDC-coated Ni/YSZ anode, the cell performance was also rapidly decreased for the first few hours, and then it fluctuated. After 15 h of introducing  $\text{CH}_4$ , the cell performance reached a quasi-equilibrium state at 0.65 V. The reactions of the electrochemical oxidation of methane, methane pyrolysis, and deposited carbon electrochemical oxidation could be competed in the fluctuating stage, and then they are equilibrated. At the equilibrium stage, the electrochemical oxidation of methane was the governing reaction mechanism in the anode, due to the MIEC and active electro-catalytic properties of SDC, the additional TPB area, and the SDC covering effects. The exposure of the Ni phase to methane could be reduced by the SDC coating layer, which could limit the methane pyrolysis via reaction (2), leading to low carbon deposition.



**Fig. 6** IV characteristics for the Ni/YSZ anode and the SDC-coated Ni/YSZ anode in  $\text{H}_2$  conditions (a) and  $\text{CH}_4$  conditions (b) at  $800^\circ\text{C}$



**Fig. 7** Comparisons of the cell performance under  $\text{CH}_4$  conditions at  $800^\circ\text{C}$  with a constant current of  $0.1 \text{ A cm}^{-2}$  for the Ni/YSZ anode and the SDC-coated Ni/YSZ anode

Figure 8 shows the SEM images of the unmodified Ni/YSZ anode and the SDC-coated Ni/YSZ anode after long-term testing in  $\text{CH}_4$ . The cell was cooled to room temperature in  $\text{N}_2$  to avoid oxidation of the carbon, and the carbon deposition on the anode was analyzed. For the

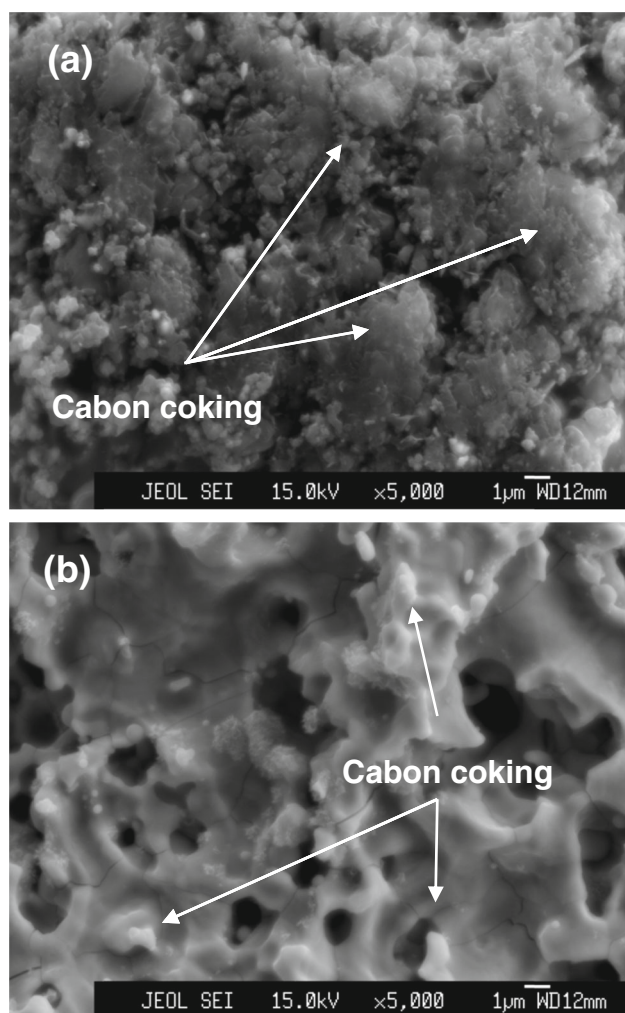
unmodified Ni/YSZ anode, a significant amount of bulk carbon was detected, which could affect the cell performance drop, as shown in Fig. 7. The bulk carbon formation could block the anode and deactivate the electrochemical property of the anode. For the SDC-modified Ni/YSZ anode, a little carbon coking was still found, which the polarization resistance could cause increase the polarization resistance as shown in Fig. 5b. Detailed electrochemical impedance spectroscopy analysis is very difficult under  $\text{CH}_4$  condition in the SDC-coated Ni/YSZ anode because the reaction mechanisms are complicated. Direct electrochemical oxidation of  $\text{CH}_4$  could be competed to  $\text{H}_2$  via direct electrochemical oxidation or steam reforming of  $\text{CH}_4$ . Also, CO could be associated. In addition, deposited carbon on the anode surface could affect to the polarization resistance in several ways depending on the amount of carbon deposition. Electronically conductive property of

the deposited carbon on the surface of the anode might decrease the polarization resistance initially which could affect IR resistance or ohmic resistance in high frequency region. Also, the carbon deposition on the Ni surface could decrease the electro-catalytic property of Ni. Bulk carbon formation could be the major cause of the increased resistance for gas phase diffusion by blocking pore or decreasing pore size. The electrochemical oxidation of methane via reaction (1) and the electrochemical oxidation of carbon via reaction (3) could likely occur in the SDC-coated Ni/YSZ anode, leading to the relatively stable cell performance, as shown in Fig. 7.

#### 4 Conclusions

To develop an alternative anode for SOFCs for use with methane fuel, SDC was coated on a Ni/YSZ pore wall surface and compared to a conventional Ni/YSZ anode. The porous SDC thin layer was applied to the anode using a sol-gel coating method. The experiment was performed in  $\text{H}_2$  and  $\text{CH}_4$  conditions at 800 °C. For the SDC-coated Ni/YSZ anode, the cell performance was improved by approximately 20 % in  $\text{H}_2$  conditions due to the high ionic conductivity of the SDC, the MIEC property of the SDC, and the additional TPB area by SDC coating in the anode. In  $\text{CH}_4$  conditions, the cell performance of the unmodified Ni/YSZ anode was severely reduced because of bulk carbon formation. The pyrolysis of methane was the governing reaction mechanism in the anode, which deactivated the electro-catalytic property of the anode, and blocked the anode pores, leading to decreased cell performance. For the SDC-coated Ni/YSZ anode, the carbon was unlikely to be deposited in the anode. The electrochemical oxidation of methane could be the governing reaction mechanism in the anode due to the high ionic and MIEC properties of the SDC. The whole coverage of the porous SDC thin layer could reduce the exposure of the Ni phase to  $\text{CH}_4$ , leading to limitation of the  $\text{CH}_4$  pyrolysis. The cell performance of the SDC-coated Ni/YSZ anode did not show any significant degradation up to 90 h under  $0.1 \text{ A cm}^{-2}$  at 800 °C. This stands in contrast to the critical degradation observed in the unmodified Ni/YSZ anode. Consequently, the porous thin SDC coating on the Ni/YSZ anode provided the electrochemical oxidation of  $\text{CH}_4$  over the whole anode and minimized the carbon deposition by electrochemical carbon oxidation. Moreover, the porous SDC coating layer provided an additional TPB area, resulting in improvement in the cell performance.

**Acknowledgments** This study was financially supported by Chonnam National University, 2011.



**Fig. 8** Carbon deposition of scanning electron microscopy images on the surface of the Ni/YSZ anode (a) and the SDC-coated Ni/YSZ anode (b)

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